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(54) Title: HEAT TRANSFER ELEMENT (57) Abstract The invention relates to a heat transfer element for use in the manufacture of radiant panels for power generating stations. The heat transfer element comprises a rigid base portion providing structural strength and a fluoropolymer coating which protects the base portion from physical and chemical corrosion whilst providing anti-fouling properties and good flow characteristics to the element. A thermally conductive material is distributed within the element to provide the necessary heat transfer characteristics.		

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HEAT TRANSFER ELEMENT

Background of the Invention

1. Field of the Invention

The present invention relates to a heat transfer
5 element, more particularly to a heat transfer element for
use in a power generating station or a chemical processing
plant.

2. Background

There are currently over six hundred power generating
10 stations in the European Union. An important feature of
these stations is the provision of heat exchangers
consisting of a number of radiant panels which serve to
transfer heat within the station. There may be around
30,000 square metres of radiant panels in a single heat
15 exchanger. A power generating station may use up to
twelve or more heat exchangers.

The radiant panels should not only serve their
primary heat transfer function, they should also be robust
to withstand the conditions in which they operate. Thus,
20 not only are physical conditions harsh, with hot gas, e.g.
furnace exhaust gases, and steam at up to about 150°C
flowing at high speed past the panels, but also corrosive
chemicals, such as sulphurous and nitrous acids, may be
present in the hot gas stream. Furthermore, the panels
25 may become clogged with soot or debris, which may also
impair their function. The panels are also subjected to
rapid thermal cycling.

Conventionally, heat transfer elements used to make
the radiant panels have been manufactured from a metal
30 with a vitreous enamel coating. The metal base material,
conveniently of mild steel, provides the necessary
structural strength to the element and also the required
thermal conductivity. A coating of vitreous enamel
protects the metal base from the corrosive effects of the
35 surrounding environment. Recently, attempts have been
made to provide heat transfer elements by spraying a metal
base with a fluoropolymer. However, the resulting

composite element is not economical to manufacture.

In United States Patent No. 5,616,388 there is disclosed a solventless process for preparing a fluoropolymer based coating which involves mixing and heating a fluoropolymer with a thermoplastic acrylic resin to obtain a molten mixture, slowly cooling the molten mixture to obtain a solid mass having a degree of crystallinity of at least 85% and grinding the solid mass at a temperature higher than -50°C.

United States Patent No. 5,562,156 discloses an immersion type heat exchanger with a fluorocarbon coating. Such a heat exchanger will not be exposed to temperatures in excess of about 100° C in use. The fluorocarbon coating on the heat exchanger can be produced by powder coating followed by burning.

Laminates of a polymer having perfluorocyclobutane rings with another layer which may be any material are described in United States Patent No. 5,409,777. Use of the perfluorocyclobutane ring-containing polymers as powder coatings in the electrical and electronics industries is proposed.

European Patent Specification No. 0445523A mentions that polymer compositions with high thermal conductivity can be used in articles such as heat exchange tubing and heated cable jackets and discusses incorporation of conductive particles of carbon black or graphite or graphite fibres in polymers. There is also a suggestion to add to a melt-processable tetrafluoroethylene copolymer of a specific type graphite fibres, metal powders and granules, a metal oxide such as iron oxide, zinc oxide, aluminium oxide and magnesium oxide and silicon carbide.

United States Patent No. 4,461,347 discloses a heat exchange assembly including a metal pipe on which is shrink fitted a heat-shrinkable TFE tubing.

In United States Patent No. 4,452,302 there is taught a heat exchanger for use during crystallisation in which passage walls in the heat exchanger are coated with a

polymeric material layer such as a thin film bonded to the surface or passage walls by an adhesive or a layer polymerised in situ. Paint can be used.

United States Patent No. 4,193,180 is concerned with
5 a structure comprising a metal tube jacketed over the major part of its length with an extruded layer of a given fluorocarbon resin and jacketed on at least a part of the remainder of its length adjacent said extruded layer of resin with a fused sprayed on layer of said given resin of
10 which an end section is overlapped on and fused to a narrow circumferential band at the adjacent end of said extruded layer of resin.

In European Patent Specification No. 0203213A it is proposed that the plate elements of a heat exchanger
15 should be prepared by mixing graphite powder with a pulverous fluoropolymer at 200 to 350°C, cooling and comminuting the resulting product, and pressing the comminuted material on to plate elements at at least 200°C and a pressure of at least 200 bar. Such plate elements
20 can be partly reinforced by a carbon fibre structure bonded to the surface, for example with molten polyvinylidene fluoride.

There is a need to improve upon the performance of heat transfer elements in power generating stations.
25 Thus, it would be desirable to provide a heat transfer element with improved heat transfer properties, with improved anti-fouling properties, with improved resistance to physical and chemical corrosion, and with improved mechanical properties.

30 An object of the present invention is to attain some or all of these desiderata.

A further object of the present invention is to provide a heat transfer element with the improved properties referred to above but which is economical to
35 manufacture.

Summary of the Invention

According to one aspect of the present invention

there is provided a heat transfer element comprising:

a base portion of a rigid material; and

a fluoropolymer coating over the base portion, the coating being formed on the base portion by powder
5 coating;

a thermally conductive material being distributed within the heat transfer element.

The fluoropolymer coating is preferably applied by powder coating as thinly as possible so as to provide a
10 continuous coating with no pinholes therein. Preferably the coating applied in this way is no more than about 400 μm in thickness. More usually it will be in the range of from about 80 μm up to about 200 μm or more, e.g. up to about 300 μm , in thickness.

15 According to a further aspect of the present invention there is provided a heat transfer element comprising:

a base portion of a rigid material; and

a fluoropolymer coating over the base portion, the
20 coating being formed on the base portion by compression moulding or lamination;

a thermally conductive material being distributed within the heat transfer element.

It is preferred that the fluoropolymer coating formed
25 on the base portion by compression moulding or lamination shall be as thin as practicable. Preferably, the thickness of the fluoropolymer coating applied by compression moulding or lamination does not exceed about 200 μm , even more preferably the thickness of the coating
30 is between about 40 μm and about 100 μm .

One advantage of applying the coating by compression moulding or by lamination is that it enables the formation of significantly thinner fluoropolymer coatings that are substantially pinhole free on the base portion than is
35 possible by powder coating. The coating can be applied from a fluoropolymer film that is itself substantially pinhole free and is of appropriate thickness, for example

from about 40 μm up to about 120 μm , preferably from about 50 μm to about 100 μm . A further advantage is that, whereas the powder coating technique results in formation of a fluoropolymer coating with a somewhat variable
5 thickness so that the resulting coating has a somewhat uneven or rough surface, compression moulding or lamination results in a smooth coating on the heat transfer element.

The use of compression moulding or lamination thus
10 enables the production of a heat transfer element comprising:

a base portion of a rigid material; and
a continuous fluoropolymer coating over the base
portion having a substantially constant thickness which
15 does not exceed about 200 μm ;

a thermally conductive material being distributed within the heat transfer element.

The heat transfer elements of the invention have a number of significant advantages over conventional heat
20 transfer elements, in particular over the conventional elements used to form the radiant panels of power generating stations. The provision of a fluoropolymer coating significantly improves the anti-fouling properties of the heat transfer elements of the invention.

25 Fluoropolymers have low surface energy and good lubricity and are therefore able to resist fouling by soot and debris to a greater extent than has been the case with conventional ceramic materials. Furthermore, fluoropolymers tend to be extremely resistant to chemical
30 attack and are well adapted to withstand the corrosive action of the sulphurous and nitrous acids present in the air stream flowing past the elements when in use. This resistance to chemical attack prevents surface solvation, which could otherwise worsen the flow characteristics of
35 the surface.

Detailed Description of the Invention

The rigid base portion may itself be of a thermally

conductive material such that the distribution of thermally conductive material within the element is provided, in whole or in part, by the base portion. Thus, the base portion may for example be of mild steel or any other appropriate material which has both sufficient structural strength and thermal transfer properties.

In one preferred embodiment of the invention, the rigid base portion is meshed. For example, the rigid base portion may comprise a mild steel mesh. This arrangement provides structural strength whilst limiting the weight of the element. The thickness of the rigid base portion is typically from about 400 μm to about 5 mm, preferably from about 400 μm to about 2 mm.

One advantage of using a thermally conductive material as the base portion is that it may not then be necessary to provide any further thermally conductive material in the element. In this case, the base portion will itself serve as the sole thermally conductive material in the element. However, it may in some cases be preferred to distribute a thermally conductive material within the element elsewhere than in the base portion. Thus, in one preferred embodiment of the invention, the thermally conductive material comprises a particulate or filamented material, for example, a particulate or filamented metal such as iron or steel. Thus the thermally conductive material may comprise steel or iron powder or short lengths of steel or iron wire. This particulate or filamented material may be mixed with the fluoropolymer prior to powder coating, compression moulding or lamination. The resulting heat transfer element according to the invention will comprise a rigid base material, which may if desired be of metal or some other thermally conductive material but which may alternatively be made from a thermal insulator, such as a rigid plastics material or ceramic material, and a fluoropolymer coating having the thermally conductive particulate or filamented material distributed within the

fluoropolymer coating.

In another preferred embodiment of the invention, an intermediate layer of a plastics material is provided between the base portion and the fluoropolymer coating.

5 The plastics material should be compatible with the base portion and the fluoropolymer coating and is preferably an acrylic polymer or alloy. This arrangement may be particularly preferred when the base portion does not have a flat surface, for example when the base portion is

10 meshed. In this case, the use of a relatively (compared to the fluoropolymer) inexpensive intermediate layer of acrylic polymer means that on powder coating, compression moulding or lamination of the co-laminate the thermoplastic acrylic polymer flows into the wells of the

15 meshed base portion and provides a relatively flat surface upon which the fluoropolymer adheres.

When the fluoropolymer coating is formed by powder coating the particle size of the fluoropolymer powder used for coating is preferably such that $D(v, 0.1)$ is from $10\mu\text{m}$ to $30\mu\text{m}$, preferably from $12\mu\text{m}$ to $18\mu\text{m}$, for example about $15\mu\text{m}$; $D(v, 0.5)$ is from $30\mu\text{m}$ to $70\mu\text{m}$, preferably from $35\mu\text{m}$ to $45\mu\text{m}$, for example about $40\mu\text{m}$; and $D(v, 0.9)$ is from $60\mu\text{m}$ to $130\mu\text{m}$, preferably from $70\mu\text{m}$ to $86\mu\text{m}$, for example about $78\mu\text{m}$. (By " $D(v, x)$ is $y\mu\text{m}$ " is meant that the

20 particle size distribution is such that 100x% of the particles in the coating composition are less than $y\mu\text{m}$ in diameter.)

The use of powder coating in the heat transfer elements of the invention allows the fluoropolymer coating to be formed relatively evenly and relatively thinly over the base portion. The thickness of the fluoropolymer coating over the base portion is preferably as low as possible, consistent with a substantial lack of pinholes in the coating. By keeping the coating thickness as low

30 as possible, the thermal transfer properties of the element can be improved while allowing cost-effective manufacture of the element by minimising the quantity of

35

the expensive fluoropolymer used in the coating.

Preferably, the thickness of the coating does not exceed about 400 μm , and preferably is no more than about 200 μm .

Even more preferably the thickness of the coating, when
5 applied by powder coating, is between about 80 μm and about 200 μm .

The use of compression moulding or lamination, for example continuous belt lamination, to form the fluoropolymer coating over the base portion allows the
10 manufacturer to minimise the thickness of the coating, thus improving the thermal transfer properties of the element and allowing cost-effective manufacture of the element by minimising the quantity of the expensive fluoropolymer used in the coating. Moreover it permits
15 the manufacture of heat transfer elements with a smoother finish than is attainable by powder coating. Preferably, the thickness of the fluoropolymer coating, when applied by compression moulding or lamination, using a fluoropolymer film in either case, does not exceed about
20 200 μm , even more preferably the thickness of the coating is between about 40 μm and about 100 μm .

The fluoropolymer used in the present invention is preferably a fluorohydrocarbon polymer, such as polyvinylidene fluoride (PVDF) or a copolymer with at
25 least 80% by weight of vinylidene fluoride and up to 20% by weight of at least one other fluorine based monomer. Suitable fluorine based monomers which may be used with vinylidene fluoride are tetrafluoroethylene, hexafluoropropylene and vinylfluoride, having the
30 characteristics listed in United States Patents Nos. 4,770,939 and 5,030,394. The fluoropolymer is most preferably PVDF and is commercially available from Atochem North America, Inc. under the trade designation KYNAR 500 PC, KYNAR 710, KYNAR 711 or KYNAR 2800. Other
35 fluoropolymers which may be mentioned include PFA resins, i.e. tetrafluoroethylene-perfluoroalkoxyethylene copolymers.

The fluoropolymer may be mixed with another thermoplastic polymer. The preferred thermoplastic polymers are acrylic polymers with units derived from acrylates or methacrylates, such as copolymers derived
5 from an alkyl acrylate or alkyl methacrylate, preferably, methyl methacrylate or from at least one other olefinically unsaturated monomer. Acrylic acid and methacrylic acid are also suitable as the other olefinically unsaturated monomer. Advantageously, the
10 copolymers comprise at least 75% by weight of units derivable from an alkyl methacrylate and up to 25% by weight of units derivable from one or more other olefinically unsaturated monomers. The thermoplastic polymer is preferably poly(methyl acrylate) or poly
15 (methyl methacrylate) or an alkyl methacrylate/alkyl acrylate copolymer. These thermoplastic polymers have the characteristics listed in United States Patents Nos. 4,770,939 and 5,030,394 and are commercially available from Rohm & Haas Company under the trade description
20 Acryloid/Paraloid B-44®. These materials are described in United States Patent No. 5,229,460. Another preferred acrylic polymer is available from Atohaas under the trade designation OROGLAS HFI-10.

The use of an acrylic polymer in admixture with the
25 fluoropolymer can improve the wetting properties of the material and thus help to ensure even coating of the base material in the heat exchange element of the invention.

The weight ratio of the fluoropolymer to the thermoplastic acrylic polymer, if used, is preferably in
30 the range of from about 90:10 to 40:60, preferably from about 75:25 to 65:35, for example about 70:30.

A low melting point fluorine-based terpolymer may also be added to the fluoropolymer/thermoplastic acrylic polymer mixture. A terpolymer is a polymer made from
35 three monomers. Such a low melting point terpolymer would have, for example, a melting point of not higher than 150°C. A suitable terpolymer is vinylidene fluoride-

tetrafluoroethylene-hexafluoropropylene, having a melting temperature of about 87° to 93°C and a melt viscosity of about 11,000 to 13,000 Poise at 125°C. The preferred terpolymer is commercially available from Atochem, North America, Inc. under the trade designation KYNAR ADS®. The weight ratio of the fluoropolymer to the terpolymer, if used, is in the range of from about 50:50 to 99:1.

The mixture may also contain other additives, such as corrosion inhibiting pigments, dry flow promoting agents, antioxidants, adhesion promoters and ultra-violet-absorbing materials, although not required. One preferred additive is an antioxidant, such as 2,2-bis[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl]-1,3-propanediyl 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzene-propanoate, available from Ciba-Geigy under the trade designation Irganox 1010.

In order that the invention may be properly understood and fully carried into effect, a number of preferred embodiments thereof will now be more particularly described in the following Examples. Examples 1 to 4 describe a powder coating technique which results in fluoropolymer coatings with a matt and somewhat roughened surface with a variable thickness of between about 200 µm and about 400 µm. On the other hand Examples 5 to 8 illustrate the use of a compression moulding or lamination technique which resulted in heat transfer elements having a smoother surface finish and with a much more uniform and thinner coating than those obtained using Examples 1 to 4. The thickness of such coatings ranged from about 50 µm up to about 100 µm. The mild steel mesh used in the Examples had a thickness of 600 µm and an open area corresponding to about 50% of the surface area thereof.

Example 1

A fluoropolymer coating composition comprising the following ingredients was prepared:

Raw Materials	% by weight
Kynar™ 710	69.5%
Kynar™ ADS	5.9%
Paraloid™ B-44 Beads	29.5%
Irganox™ 1010	1.0%
Shepherd B12#20 Brown	11.6%
Shepherd BK#1 Black	1.2%
Shepherd YL#29 Yellow	0.4%
DuPont R-960 White	0.4%

The materials were mixed in a high speed MIXACO™ mixer and fed into a twin screw extruder and extruded at about 200°C. The extrudate was discharged into trays and cooled to produce blocks.

The cooled blocks were granulated into granules of from about 2 mm to about 4 mm in diameter and these granules were ground in a chilled mill to produce a powder with particle size range $D(v, 0.1)$ less than 15 μm , $D(v, 0.5)$ less than 40 μm and $D(v, 0.9)$ less than 78 μm .

The resulting powder was sprayed onto a mild steel mesh which had been pre-heated to about 240°C in an electric oven. The coated mesh was then cured sufficiently to cause the coating to reflow to form an even coating.

After cooling, the resulting heat transfer element had excellent heat transfer, anti-fouling, structural and flow characteristics.

Example 2

A fluoropolymer powder coating composition was prepared according to the method described in Example 1 from the following ingredients:

Raw Materials	% by weight
Kynar™ 710	69.3%
Paraloid™ B-44 Beads	29.7%
Irganox™ 1010	1.0%

5 The resulting powder composite was used to coat a mild steel mesh according to the method described in Example 1.

10 The resulting heat transfer element has excellent heat transfer, anti-fouling, structural and flow characteristics.

Example 3

15 A fluoropolymer powder coating composition as specified in Example 2 was prepared and mixed with stainless steel filings in a ratio of three parts by weight of the coating composition to one part by weight of stainless steel filings. The resulting composite material then coated onto a mild steel mesh as described in Example 1 to form a heat transfer element with excellent heat transfer, anti-fouling, structural and flow characteristics.

Example 4

25 A fluoropolymer powder coating composition was prepared according to the method described in Example 1 from the following ingredients:

Raw Materials	% by weight
Kynar™ 2800	60.00%
Oroglas™ HFI-10	40.00%

30 The resulting powder composite was used to coat a mild steel mesh according to the method described in Example 1 and the resulting heat transfer element had excellent heat transfer, anti-fouling, structural and flow characteristics.

Example 5

A fluoropolymer coating composition comprising the following ingredients was prepared:

Raw Materials	% by weight
Kynar™ 710	69.3%
Paraloid™ B-44 Beads	29.7%
Irganox™ 1010	1.0%

The materials were mixed in a high speed MIXACO™ mixer and fed into a twin screw extruder and extruded at about 200°C. The extrudate was quenched in a water bath and then pelletised.

The pelleted composition was extruded through a single screw extruder with a single slot die to form a continuous film with a thickness of around 120 µm.

The resulting film was used to coat a mild steel mesh with a thickness of 600 µm by placing a sheet of film on each side of the mesh and subjecting the covered mesh to a temperature of 200°C and a pressure of 0.625 tonnes per square inch (95 bar) in a heating press.

The resulting heat transfer element has excellent heat transfer, anti-fouling, structural and flow characteristics.

Example 6

A film of fluoropolymer coating composition was prepared as described above in Example 5 and was used to coat a mild steel mesh by covering both sides of the mesh with film and passing the covered mesh through a twin belt laminator. Acetate release sheets were placed over the fluoropolymer film to prevent adherence of the fluoropolymer to the belts of the laminator.

The resulting heat transfer element has excellent heat transfer, anti-fouling, structural and flow characteristics.

Example 7

A fluoropolymer coating composition as specified in

Example 5 was prepared and mixed with stainless steel filings in a ratio of three parts by weight of the coating composition to one part by weight of stainless steel filings. The resulting composite material was laminated onto a mild steel mesh as described in Example 6 to form a heat transfer element with excellent heat transfer, anti-fouling, structural and flow characteristics.

Example 8

Raw Materials	% by weight
Kynar™ 2800	60.00%
Oroglas™ HFI-10	40.00%

Examples 5 to 7 were repeated using these ingredients in place of those specified in Example 5 and in each case a heat transfer element with excellent heat transfer, anti-fouling, structural and flow characteristics was produced.

The heat transfer elements of Examples 1 to 8 are produced in the form of flat plate-like elements but can readily be bent to any desired shape prior to assembly into a heat exchanger.

CLAIMS:

1. A heat transfer element comprising:
a base portion of a rigid material; and
5 a fluoropolymer coating over the base portion, the coating being formed on the base portion by powder coating;
a thermally conductive material being distributed within the heat transfer element.
- 10 2. A heat transfer element according to claim 1, wherein the fluoropolymer coating has a thickness in the range of from about 80 μm up to about 300 μm .
- 15 3. A heat transfer element comprising:
a base portion of a rigid material; and
a fluoropolymer coating over the base portion, the coating being formed on the base portion by compression
moulding or lamination;
20 a thermally conductive material being distributed within the heat transfer element.
4. A heat transfer element comprising:
a base portion of a rigid material; and
25 a continuous fluoropolymer coating over the base portion having a substantially constant thickness which does not exceed about 200 μm ;
a thermally conductive material being distributed within the heat transfer element.
- 30 5. A heat transfer element according to claim 3 or claim 4, wherein the fluoropolymer coating has a thickness in the range of from about 40 μm to about 100 μm .
- 35 6. A heat transfer element according to any one of claims 1 to 5, wherein the base portion is of a thermally conductive material such that the distribution of

thermally conductive material within the heat transfer element is provided, in whole or in part, by the base portion.

5 7. A heat transfer element according to claim 6, wherein the base portion is of mild steel.

8. A heat transfer element according to any one of claims 1 to 7, wherein an intermediate layer of a plastics material is provided between the base portion and the
10 fluoropolymer coating.

9. A heat transfer element according to claim 8, wherein the plastics material is an acrylic polymer.
15

10. A heat transfer element according to any one of claims 1 to 9, wherein the thermally conductive material comprises a particulate or filamented material.

20 11. A heat transfer element according to claim 10, wherein the particulate or filamented material is a metal.

12. A heat transfer element according to any one of claims 1 to 11, wherein the base portion is meshed.
25

13. A heat transfer element according to any one of claims 1 to 12, wherein the fluoropolymer comprises PVDF.

14. A heat transfer element according to any one of
30 claims 1 to 13, wherein the fluoropolymer is mixed with another thermoplastic polymer.

15. A heat transfer element according to claim 14, wherein the other thermoplastic polymer is an acrylic
35 polymer.

INTERNATIONAL SEARCH REPORT

Inter. .onal Application No

PCT/GB 98/03919

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 F28F19/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 F28F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 193 180 A (PRESS IRVING D) 18 March 1980 cited in the application	1,2,4-6, 13
Y	see column 1, line 24 - line 26 see column 1, line 39 - line 44 see column 3, line 18 - line 29; figure 2 ---	8,9,14, 15
Y	US 5 616 388 A (TATSUNO TADAYOSHI ET AL) 1 April 1997 see column 6, line 63 - column 7, line 10; claims ---	8,9
Y	US 5 229 460 A (YOUSUF MOHAMMED K ET AL) 20 July 1993 see column 8, line 21 - line 25; claim 1 ---	14,15
A	---	2,4,5
	-/--	

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INTERNATIONAL SEARCH REPORT

Inter. Jnal Application No

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